



## Recycling of plastic waste: Presence of phthalates in plastics from households and industry

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4 RECYCLING OF PLASTIC WASTE: PRESENCE OF  
5 PHTHALATES IN PLASTICS FROM HOUSEHOLDS AND  
6 INDUSTRY

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## 28    **Abstract**

29    Plastics recycling has the potential to substitute virgin plastics partially as a source of raw materials  
30    in plastic product manufacturing. Plastic as a material may contain a variety of chemicals, some  
31    potentially hazardous. Phthalates, for instance, are a group of chemicals produced in large volumes  
32    and are commonly used as plasticisers in plastics manufacturing. Potential impacts on human health  
33    require restricted use in selected applications and a need for the closer monitoring of potential  
34    sources of human exposure. Although the presence of phthalates in a variety of plastics has been  
35    recognised, the influence of plastic recycling on phthalate content has been hypothesised but not  
36    well documented. In the present work we analysed selected phthalates (DMP, DEP, DPP, DiBP,  
37    DBP, BBzP, DEHP, DCHP and DnOP) in samples of waste plastics as well as recycled and virgin  
38    plastics. DBP, DiBP and DEHP had the highest frequency of detection in the samples analysed,  
39    with 360 µg/g, 460 µg/g and 2700 µg/g as the maximum measured concentrations, respectively.  
40    Among other, statistical analysis of the analytical results suggested that phthalates were potentially  
41    added in the later stages of plastic product manufacturing (labelling, gluing, etc.) and were not  
42    removed following recycling of household waste plastics. Furthermore, DEHP was identified as a  
43    potential indicator for phthalate contamination of plastics. Close monitoring of plastics intended for  
44    phthalates-sensitive applications is recommended if recycled plastics are to be used as raw material  
45    in production.

46    **Keywords:** Compositional data; Contaminants; Endocrine-disrupting chemicals (EDCs); Quality  
47    recycling; Solid waste

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49    **Abbreviations**

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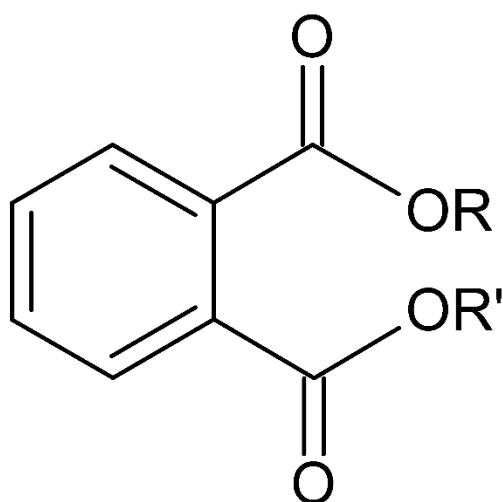
- 50    BBzP; Butyl benzyl phthalate (CAS 85-68-7)
- 51    DBP; Dibutyl phthalate (CAS 84-74-2)
- 52    DCHP; Dicyclohexyl phthalate (CAS 84-61-7)
- 53    DEHP; Diethylhexyl phthalate (CAS 117-81-7)
- 54    DEP; Diethyl phthalate (CAS 84-66-2)
- 55    DiBP; Di-iso-butyl phthalate (CAS 84-69-5)
- 56    DMP; Dimethyl phthalate (CAS 131-11-3)
- 57    DnOP; Di-n-octylphthalate (CAS 117-84-0)
- 58    DPP; Dipropyl phthalate (CAS 131-16-8)
- 59    HDPE; High-density polyethylene
- 60    HMW; High molecular weight
- 61    LOD; Limit of detection
- 62    LWM; Low molecular weight
- 63    MANOVA; Multivariate analysis of variance
- 64    PE; Polyethylene
- 65    PET; Polyethylene terephthalate
- 66    PS; Polystyrene
- 67    PVC; Polyvinyl chloride
- 68    RHP; Recycled household plastics
- 69    RIP; Recycled industrial plastics
- 70    RWP; Residual waste plastics
- 71    SSWP; Source-segregated waste plastics
- 72    VP; Virgin plastics

## 1. Introduction

Plastics are some of the most important materials for sustaining society and our current way of living (Andrady and Neal, 2009). Unfortunately, they are also associated with substantial environmental issues, as they are based primarily on non-renewable raw materials (e.g. oil), are commonly used in short-lived products (e.g. food packaging) and, once discarded, are predominantly landfilled or incinerated (Thompson et al., 2009). If not disposed of properly, waste plastics can end up in the oceans, thereby creating another environmental issue of growing concern (Jambeck et al., 2015). To tackle some of these issues, plastics recycling has been promoted within the European Union (EU). Recently proposed amendments to the directives on waste (EC, 2015a) and packaging waste (EC, 2015b) require 65% of municipal and 75% of packaging waste, including plastics, to be recycled by 2030. Nevertheless, the recycling of waste plastic is challenging due to heterogeneity of the material (e.g. polyethylene (PE), high-density polyethylene (HDPE), and polystyrene (PS)) and its chemical composition (Ignatyev et al., 2014).

Chemical composition can vary based on the plastic type (e.g. PE) or the intended use of such a product. Moreover, many hazardous chemicals can be potentially present in plastics, including phthalic acid esters, polycyclic aromatic hydrocarbons (PAHs), potentially toxic metals, etc. (NEA, 2013) Phthalic acid ethers, commonly known as ‘phthalates’, make up a group of industrial chemicals with high global production volumes. Phthalates are mostly used as plasticisers in plastics production, with polyvinyl chloride (PVC) incorporating the largest share of the market (Markarian, 2007). Although alternatives are available (Krauskopf, 2003; Markarian, 2007), phthalates still accounted for 70% of the plasticiser market in 2014, and they are forecast to account for 65% in 2019 (IHS, 2015). Phthalates can be divided into low molecular weight (LMW) and high molecular weight (HMW), whereby the former are used predominantly as solvents and in adhesives, waxes, inks, cosmetics, insecticides and pharmaceuticals, while HMW phthalates are

97 produced in higher volumes and are used in construction materials, clothing, children's toys and  
98 household furnishing (BCERC, 2007). These two groups are commonly distinguished according to  
99 the alkyl group carbon chain length (R, Figure 1). Examples of LMW (C<sub>4</sub>-C<sub>8</sub>) phthalates are diethyl  
100 phthalate (DEP), dibutyl phthalate (DBP), di-iso-butyl phthalate (DiBP) and diethylhexyl phthalate  
101 (DEHP), whereas diisononyl phthalate (DINP), diisodecyl phthalate (DIDP), diundecyl phthalate  
102 (DUP) and ditridecyl phthalate (DTDP) are commonly referred to as HMW (C<sub>9</sub>-C<sub>13</sub>).



103

104 **Figure 1.** Common structure of a phthalate molecule. R and R' denote alkyl (or aryl) group.

105 Growing concern about phthalates is related to their toxicity, in particular to their endocrine-  
106 disrupting activity (Matsumoto et al., 2008). Studies suggest that human exposure to e.g. DEHP  
107 may lead to serious effects on reproduction and development (Caldwell, 2012; Heudorf et al.,  
108 2007). Although adverse effects of high phthalate doses are relatively well documented (Martino-  
109 Andrade and Chahoud, 2010), epidemiological studies (Jurewicz and Hanke, 2011) and integrated  
110 approaches to toxicity (Kovacic, 2010) suggest potential adverse effects of even low-dose phthalate  
111 exposure and call for more data. Due to their low molecular weight, LMW phthalates are  
112 susceptible to migration from plastics, and hence they are more relevant to human toxicity (Heudorf  
113 et al., 2007). Thus, the majority of LMW phthalates are classified as substances of very high

114 concern (SVHC) in Europe, and certain restrictions on their use and applications may apply (EC,  
115 2007, 2005; EU, 2015). Similarly, US EPA issued an action plan to prioritise eight phthalates, the  
116 majority of which are LMW (USEPA, 2012).

117 The human population can be exposed to phthalates from a variety of sources, with medical  
118 devices, ingestion with food and dust constituting the major sources (Latini, 2005). As the most  
119 recent data on human exposure come from biomonitoring studies (a bottom-up approach reporting  
120 concentrations in, for example, human blood), there is still uncertainty in accounting for all the  
121 potential exposure routes and their importance to their total exposure to the population (Latini,  
122 2005; Wittassek et al., 2011). From a risk assessment perspective, this calls for better data on the  
123 presence of phthalates in potential exposure sources.

124 Although phthalate plasticisers are predominantly used in PVC (Markarian, 2007), their  
125 potential use or contamination in a variety of polymers has been previously suggested (Ionas et al.,  
126 2014; Jaworek and Czaplicka, 2014; Shen, 2005). Shen (2005) looked into a variety of polymers,  
127 including PE, PS, PVC, as well as PE laminates and cellulose-based polymers, and identified  
128 phthalates in 24 out of the 25 plastics samples analysed. Polyethylene terephthalate (PET) has been  
129 shown to leach endocrine-disrupting chemicals (EDCs), including phthalates, into water contained  
130 in PET bottles (Amiridou and Voutsas, 2011; Casajuana and Lacorte, 2003; Keresztes et al., 2013;  
131 Montuori et al., 2008; Sax, 2010; Wagner and Oehlmann, 2011). When compared to PET bottles  
132 made of virgin plastics, Keresztes et al. (2013) clearly showed higher concentrations of phthalates  
133 in water bottled in PET potentially containing 20 to 30% (w/w) of recycled PET, thus suggesting  
134 recycling of plastics as a source of phthalate contamination. The abundance of phthalates has also  
135 been identified in a number of foods coming from a variety of geographical areas (Fankhauser-Noti  
136 et al., 2006; Fierens et al., 2012; Poças et al., 2010; Schechter et al., 2013). Although packaging was  
137 identified as one source (Fankhauser-Noti et al., 2006; Wormuth et al., 2006), contamination during

138 food preparation and packaging usually cannot be ruled out, either (Tsumura et al., 2001).  
139 Additionally, use of recycled plastics and paper for food packaging was connected to possible  
140 increase in childhood exposure to selected phthalates (Lee et al., 2014). Finally, only a few studies  
141 have discussed the potential impact of plastics recycling on phthalate content, and so whether or not  
142 recycling can lead to plastic contamination and the increased presence of phthalates remains  
143 unclear.

144 The aim of the present work was to quantify selected LMW phthalates (DMP, DEP, DPP, DiBP,  
145 DBP, BBzP, DEHP, DCHP and DnOP) in samples of household waste plastics, as well as recycled  
146 and virgin plastics. Based on a consistent and comprehensive statistical data analysis methodology,  
147 the aim was further to evaluate whether the source (i.e. waste, recycled or virgin plastics) had a  
148 significant influence on phthalate content in the collected samples. Finally, the importance of  
149 plastics recycling for phthalate contamination was discussed.

## 150 2. Materials and methods

### 151 2.1 Sample collection

152 Samples of residual (RWP) and source-segregated (SSWP) waste plastics were collected from a  
153 municipality in Southern Denmark in April 2013. The sampling campaign covered 100 single-  
154 family households for a period of two weeks. Further details of the residual waste sampling are  
155 available in an earlier publication (Edjabou et al., 2015), while the same temporal and geographical  
156 scopes were applicable to the source-segregated waste samples collected. Waste samples were  
157 sorted manually in accordance to polymer resin identification codes (e.g. 1 – PET, 2 – HDPE, etc.)  
158 provided on individual plastic items. Identification codes specify of what the main polymer plastic  
159 products are made, without taking into account the presence of other materials (e.g. plastic ‘sleeves’  
160 or labels on packaging) or chemicals (e.g. glue) in the final product. To supplement the waste



161 plastic samples obtained from households, samples of processed plastics were obtained from  
162 industry. Samples of recycled household (RHP) and industrial (RIP) as well as virgin (VP) plastics  
163 were collected directly from recyclers and producers. RHP, RIP and VP samples were obtained  
164 from China, Denmark, Germany and the Netherlands, in order to illustrate potential variations in the  
165 source and quality of the material, which could result in different phthalate contents. In total, 20  
166 waste (13 for RWP and seven for SSWP) and 28 recycled (nine for RHP and 11 for RIP) and eight  
167 virgin plastic (VP) samples were collected and analysed. An overview of the samples used in the  
168 present study is provided in Table S1 (Supplementary material). In the case of recycled and virgin  
169 plastics samples, neither the precise source (apart from a general distinction between household (i.e.  
170 post-consumer) and industrial (i.e. pre-consumer)) nor the exact intended use of the final plastic  
171 product (packaging, transportation, food-contact materials, etc.) was known. The samples obtained  
172 (both waste and processed plastics) were not expected to represent the composition of plastics on  
173 the global market or in the respective countries but rather to provide a basis for evaluating the  
174 influence of plastic source on phthalate content and the potential for recycling.

## 175 *2.2 Sample pre-treatment*

176 Samples of waste plastics (i.e. RWP and SSWP) were treated by means of coarse shredding (ARP  
177 SC2000, Brovst, Denmark) followed by fine shredding (SM2000, Retsch, Germany) to a particle  
178 size  $< 1$  mm. Before being finely shredded, the samples were submerged in liquid nitrogen, in order  
179 to increase brittleness and avoid to overheating and malfunctioning the equipment used. Samples of  
180 recycled and virgin plastics (RHP, RIP and VP) were obtained in the form of granules, flakes,  
181 granulate or pellets, and they did not undergo any additional treatment before being extracted and  
182 analysed. This did not apply to sample number 28 (RHP), which was obtained in the form of an

183 extruded plastic block and which had to be ground down before extraction. The final samples were  
184 stored at room temperature in a dark and dry environment prior to extraction and chemical analysis.

### 185 *2.3 Sample extraction and chemical analysis*

186 The phthalates extraction procedure was a modified method based on selected scientific literature  
187 (Cano et al., 2002; Gawlik-Jędrysiak, 2013; Shen, 2005). For each of the samples 0.5 g of plastics  
188 were put into contact with 20 ml of dichloromethane (DCM), which was used as a solvent. Among  
189 potential alternative solvents for phthalates extraction, DCM has been shown to exhibit the highest  
190 recovery yields for plastics (Gawlik-Jędrysiak, 2013). An internal standard mix of DMP-d4 and  
191 DEHP-d4 was added to each of the samples to a final concentration of 2.5 mg/l. The extraction was  
192 performed in a microwave-assisted extraction setup (Multiwave 3000, Anton-Paar, Graz, Austria) at  
193 120°C for 20 minutes. Next, the extraction solvent was decanted, filtrated on a glass-fibre filter and  
194 evaporated to approximately 3 ml under a gentle stream of nitrogen. A solid-phase extraction (SPE)  
195 clean-up was performed on the evaporated extracts by passing extracts through a glass column  
196 containing activated Alumina-N, conditioned with DCM. The collected flow-through was analysed  
197 on a gas chromatographer coupled with a mass spectrometer (GC-MS). To avoid potential  
198 contamination of extracts and resulting blank problems with the phthalates analysis (Fankhauser-  
199 Noti and Grob, 2007), all glassware used in the extraction was rinsed in acetone and dried overnight  
200 at 200°C before being used.

201 Chromatographic separation was achieved on an Agilent 6890 gas chromatograph (Agilent  
202 Technologies, Santa Clara, USA) equipped with a 60 m x 0.25 mm i.d. x 0.25 µm film thickness  
203 ZB-5ms column with a 5 m guard column (Phenomenex, Torrance, USA). The samples were  
204 injected in splitless mode, with the sample inlet held at 300°C. The oven was programmed to 70°C  
205 for 3 mins and then ramped at 13°C/min to 270°C, then at 50°C/min to 300°C and finally held for

12 minutes. Helium was used as a carrier gas with a 1 ml/min constant flow. Detection was achieved on an Agilent 5975C triple-axis mass-selective detector (Agilent Technologies, Santa Clara, USA) operated in selected ion-monitoring (SIM) mode, with the MS source at 230°C and the quadrupole at 150°C. The detection limits achieved ranged from 0.036 µg/g (DPP) to 3.4 µg/g (DEP). Detailed detection limits for each of the phthalates are provided in Table 1.

In order to validate the analytical method and instruments used during the analysis, a standard reference material was used. A standard of three phthalates (DBP at 963 µg/g, BBP at 962 µg/g and DEHP at 1018 µg/g) in polypropylene (PP) resin pellets was accompanied by the reference material certificate from National Metrology Institute of Japan (NMIJ CRM 8151-a). Recoveries obtained for the three phthalates analysed in the standard were  $141 \pm 6\%$ ,  $90 \pm 5\%$  and  $99 \pm 2\%$  for DBP, BBP and DEHP, respectively. Additionally, each batch of samples ( $n = 15$ ) was accompanied by a DCM blank, the response of which was subtracted from the results for the respective batch.

#### 2.4 Statistical analysis

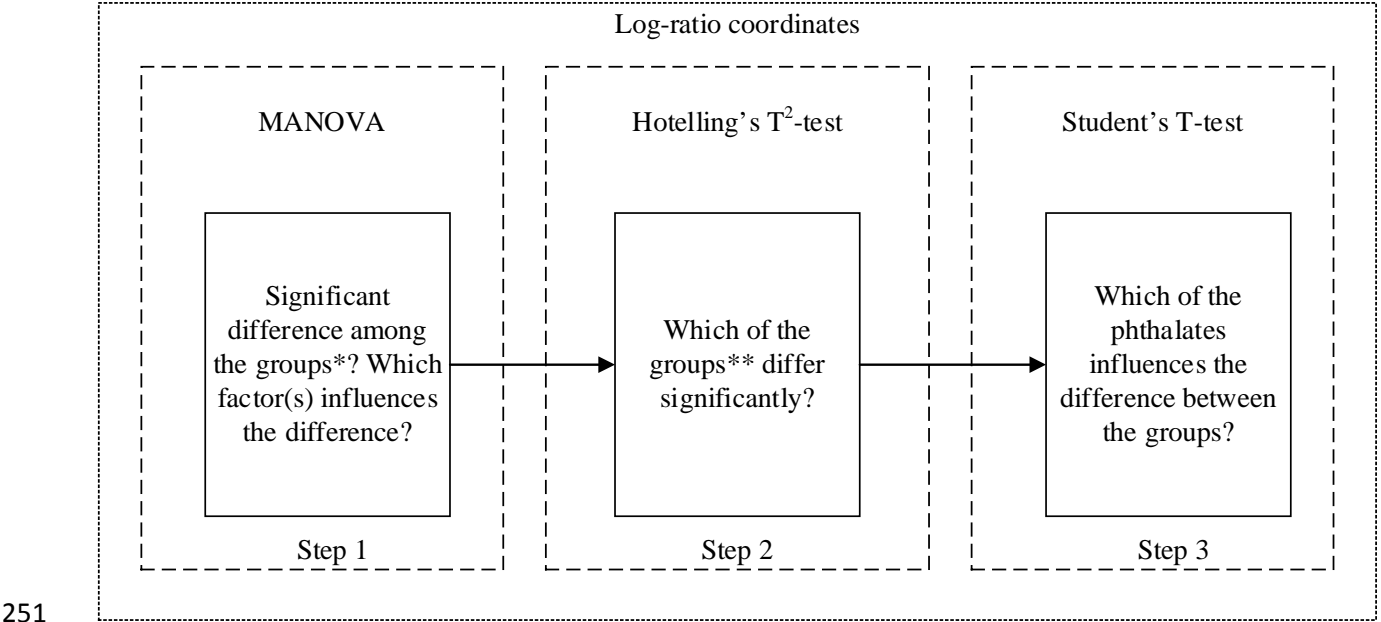
Statistical analysis of experimental data was performed in three steps, following the comprehensive methodology illustrated in Figure 2. Data conversion and analysis were performed using freely available software for compositional data analysis (available at <http://www.compositionaldata.com>) and statistical computing and graphics (available at <https://www.r-project.org>). In order to apply the proposed statistical methodology, the evaluated dataset was transformed into isometric log-ratio (ilr) coordinates on an orthonormal basis (Egozcue et al., 2003). This approach avoids potential problems related to assuming normal distribution of the original experimental data (Limpert and Stahel, 2011). Importantly, the multivariate techniques applied in this study are invariant under change of basis (Martín-Fernández et al., 2015). For interpretation purposes, the log-ratio coordinates computed for a given data subset, comprising, for example, DiBP, DBP and DEHP,

were as follows (the formulas are not simplified, in order to highlight the consistency of the expressions):

$$\begin{cases} ilr_1 = \sqrt{\frac{2 \cdot 1}{2+1}} \cdot \log\left(\frac{{}^2\sqrt{DiBP \cdot DBP}}{{}^1\sqrt{DEHP}}\right) \\ ilr_2 = \frac{\sqrt{1 \cdot 1}}{\sqrt{1+1}} \cdot \log\left(\frac{{}^1\sqrt{DiBP}}{{}^1\sqrt{DBP}}\right) \end{cases} \quad \text{Eq. (1)}$$

Normality of the log-ratio coordinates was assured through a Shapiro-Wilk test, assuming a 95% confidence interval when accepting or rejecting the null hypothesis. A multivariate analogy of the Shapiro-Wilk test was used to assess the multivariate normality of data distribution (Korkmaz et al., 2014). A two-way multivariate analysis of variance (MANOVA) for the log-ratio coordinates (Martín-Fernández et al., 2015) was performed, in order to evaluate the influence of two factors, namely the source of the plastic samples (waste plastics, recycled industrial plastics, etc.) and plastic resin (PET, PP, PS, etc.), on phthalate content (Figure 2, Step 1). As the dataset was unbalanced (i.e. an unequal number of samples across RWP, SSWP, RHP, RIP and VP), MANOVA was based on the Type II sum of squares approach (Langsrud, 2003). In case significant differences were detected by the MANOVA test, a multivariate multiple comparison test (Hotelling's  $T^2$ -test (Curran, 2013)) was performed (Figure 2, Step 2). The test's results indicated which of the data groups (grouping was based on those factors with significant influence, as identified by MANOVA test) were significantly different. Finally, a pairwise t-test (Student's T-test (Winter, 2013)) was performed, in order to identify the phthalates responsible for the significance of differences between given groups (Figure 2, Step 3). The results of the Hotelling's and Student's tests ( $p$ -values) were put in table format and are provided in the results and discussion section. For the purpose of statistical analysis, values under the detection limit in the used dataset were replaced

249 with 65% of the respective detection limit, following an approach suggested by Palarea-Albaladejo  
 250 and Martín-Fernández (2015).



252 **Figure 2.** Flowchart of the statistical methodology applied in experimental data analysis. Each of  
 253 the steps (Step 1, 2 and 3) was designed to provide answers on the questions outlined in the  
 254 respective boxes. \*grouping according to the source of plastics (factor 1), plastic resin (factor 2) or  
 255 the combination of two factors; \*\*grouping according to the factor(s) with significant influence, as  
 256 identified in Step 1.

257

### 3. Results and Discussion

#### 3.1 Analytical results

Detailed concentrations of all the phthalates analysed, including triplicates for each of the samples, are presented in Tables S2-S6 (Supplementary material). Concentration ranges (min and max) for each of the phthalates are presented in Table 1, together with the respective limits (LOD) and frequency (FOD) of detection.

**Table 1.** Ranges of phthalate concentrations as measured in the samples of plastics and rounded to two significant figures [ $\mu\text{g/g}$ ]. “<” indicates values lower than the respective limit of detection (LOD).

$\mu\text{g/g}$	DMP		DEP		DPP		DiBP		DBP		BBzP		DEHP		DCHP		DnOP	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
LOD	0.077		3.4		0.036		0.20		0.094		0.022		0.43		0.16		0.20	
RWP	<	120	<	150	<	4.3	<	460	<	190	<	92	1.2	860	<	0.72	<	99
SSWP	<	0.54	<	5.5	<	0.36	<	23	0.56	360	<	1.1	<	2700	<	<	<	2.0
RHP	<	3.4	<	6.3	<	<	<	23	<	11	<	15	<	600	<	2.5	<	31
RIP	<	0.22	<	19	<	0.47	<	7.1	<	12	<	0.36	<	17	<	<	<	0.38
VP	<	<	<	5.3	<	0.44	<	4.8	<	15	<	0.21	<	21	<	0.34	<	0.75
FOD*	19		11		14		86		93		36		79		4		20	

Among the 144 replicates analysed (48 samples x 3 replicates), DBP, DiBP and DEHP were quantified with the highest frequency. On the other hand, DCHP, DEP and DPP were only present in a few of the analysed samples. Ionas et al. (2014) also showed that DPP and DnOP had the lowest frequency of detection among the plastic samples they analysed ( $n = 50$ ). Limited use of DPP was also highlighted by not detecting it in any of the house dust samples analysed ( $n = 29$ ) in the United Kingdom (Greenpeace, 2003). In our case, the highest concentrations measured were for DEHP (max 2700  $\mu\text{g/g}$  in SSWP), which was almost three times higher than the 0.1% or 1000  $\mu\text{g/g}$

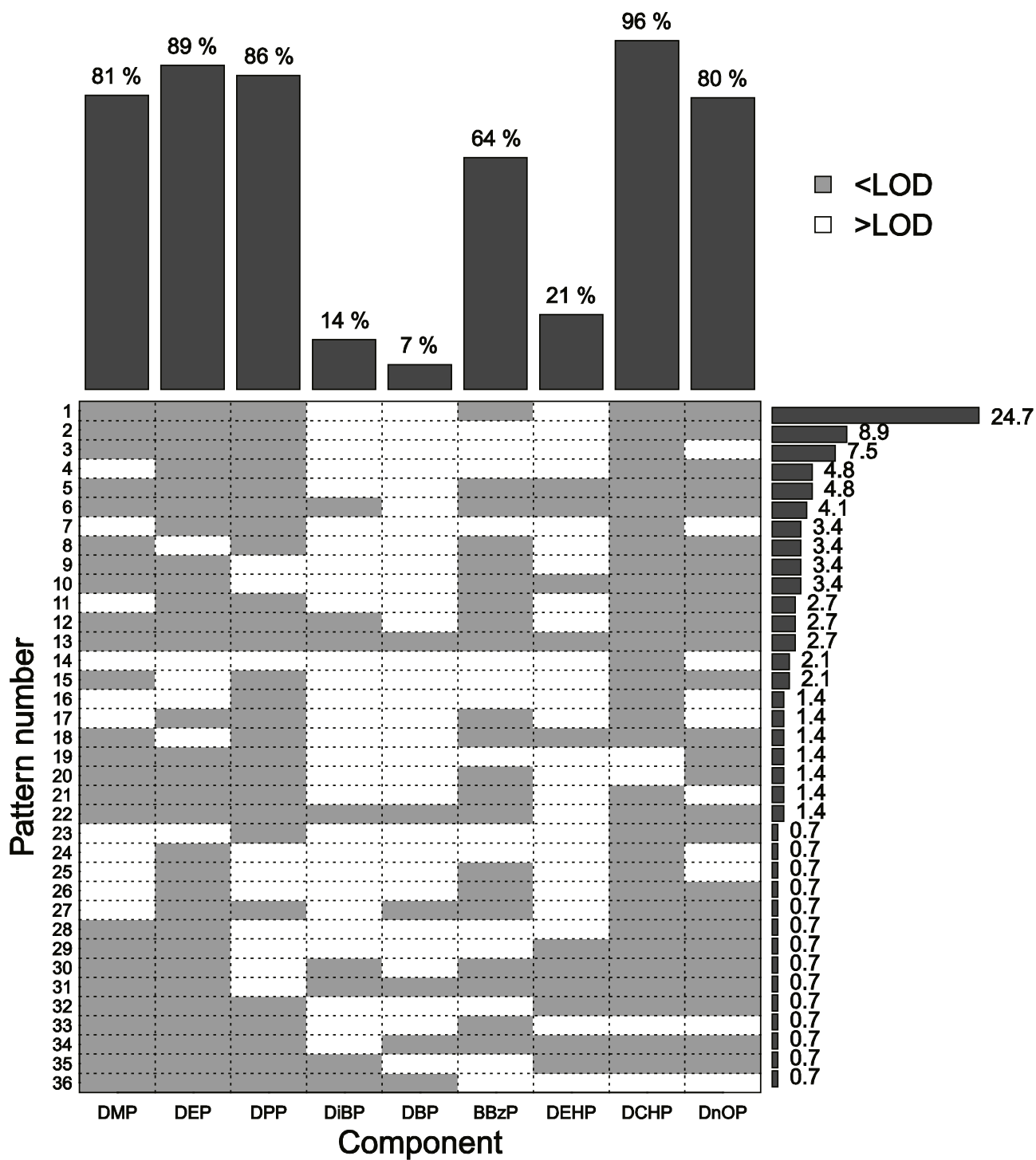
limit for plastic articles intended to come into contact with food (EC, 2007) or be used in electric and electronic equipment (EU, 2015). DEHP is considered the most commonly used plasticiser, resulting in its relative abundancy in the environment when compared to other monitored phthalates (Latini, 2005). Similarly, Shen (2005) identified DEHP in the majority of 25 samples analysed, with the highest concentration (1764 µg/g) found in a food packaging plastic bag. In accordance with Table 1, the second highest concentration was measured for DiBP (460 µg/g in RWP), which may be used as a substitute for DEHP or DBP in plastics, and which has been related to an increasing trend in human exposure based on retrospective biomonitoring data (Wittassek et al., 2007). Phthalates found in the lowest concentrations were DPP and DCHP, with 4.3 µg/g (RWP) and 2.5 µg/g (RHP) being the highest concentrations measured, respectively. Correspondingly, the highest concentration of DPP found by Ionas et al. (2014) in plastics was 2 µg/g. DPP was also among the phthalates migrating into foods from plastic packaging in the lowest concentrations (Fan et al., 2012).

### 3.2 Statistical analysis

Figure 3 summarises analytical data on the presence of phthalates in plastics. As evident from this figure and from Table 1, the majority of phthalates (six out of nine) were detected only in a few of the samples. In accordance with Helsel and Hirsch (1992), datasets with undetected values (< LOD) higher than 50% should be excluded from statistical data analysis, as they introduce considerable mathematical bias. Based on this assumption, only DiBP, DBP and DEHP were included in the statistical analysis, as these phthalates were identified at 86%, 93% and 79% frequency of detection, respectively. This corresponds to approximately 14% (DiBP), 7% (DBP) and 21% (DEHP) of samples under detection limit, as illustrated in Figure 3.

296 Results of the MANOVA test (Figure 2, Step 1) indicated that there was a significant difference  
297 (95% confidence interval) between plastics originating from the five sources (i.e. RWP, SSWP,  
298 RHP, RIP and VP). On the other hand, neither the plastic resin nor the combination of the sample  
299 source and plastic resin appeared to have a significant influence on phthalate content. Based on this  
300 conclusion, only the source of plastic samples was evaluated as an influencing factor in the ensuing  
301 steps of the statistical analysis. A summary of the MANOVA test results is provided in Table S7  
302 (Supplementary material).





303

304 **Figure 3.** Summary of detected (> LOD) vs undetected (< LOD) phthalates in the total of the  
 305 dataset (Palarea-Albaladejo and Martín-Fernández, 2015). Bars on the top represent percentage  
 306 distribution of undetected values to the total of a column. Bars on the right represent the percentage  
 307 distribution of the patterns appearing in the table (e.g. top bar indicates that approximately 25% of

all the samples analysed showed DMP, DEP, DPP, BBzP, DCHP and DnOP in values < LOD, while DiBP, DBP and DEHP were > LOD).

The results of Hotelling's  $T^2$ -test (Figure 2, Step 2) are presented in Table 2. As evident from the table, waste plastics (RWP and SSWP) as well as RHP had no significant difference as to the phthalate content ( $p$ -value > 0.05). On the other hand, all three groups of household plastics (RWP, SSWP and RHP) showed higher phthalate content and were significantly different ( $p$ -value < 0.05) from the recycled industrial (RIP) and virgin plastics (VP). Finally, recycled industrial and virgin plastics were similar in phthalate content ( $p$ -value > 0.05). Overall, and based on the analysed samples, these results may suggest that phthalates are not removed during the recycling of household (i.e. post-consumer) plastics, which could lead to them spreading and accumulating despite the fact that some phthalate losses do occur in, for example, the mechanical re-processing of plastics (Huang et al., 2013). Furthermore, the similarity between RIP and VP indicates that the recycling of industrial or pre-consumer plastics does not lead to an increase in phthalate content.

**Table 2.** Pairwise multivariate multiple comparison test. Values represent the  $p$ -values from Hotelling's  $T^2$ -test. Values lower than 0.05 indicate statistically significant difference between the two groups being compared.

	Residual waste	Source-segregated waste	Recycled (Household)	Recycled (Industrial)
Source-segregated waste	0.41	1		
Recycled (Household)	0.48	0.66	1	
Recycled (Industrial)	<0.01	<0.01	0.01	1
Virgin	0.02	0.02	0.02	0.86

Once significant differences between the groups were indicated by the Hotelling's  $T^2$ -test (see Table 2 for details), one could interpret these differences in terms of phthalate content. The groups identified as being different in Step 2 were compared by means of a Student's T-test (Step 3). The

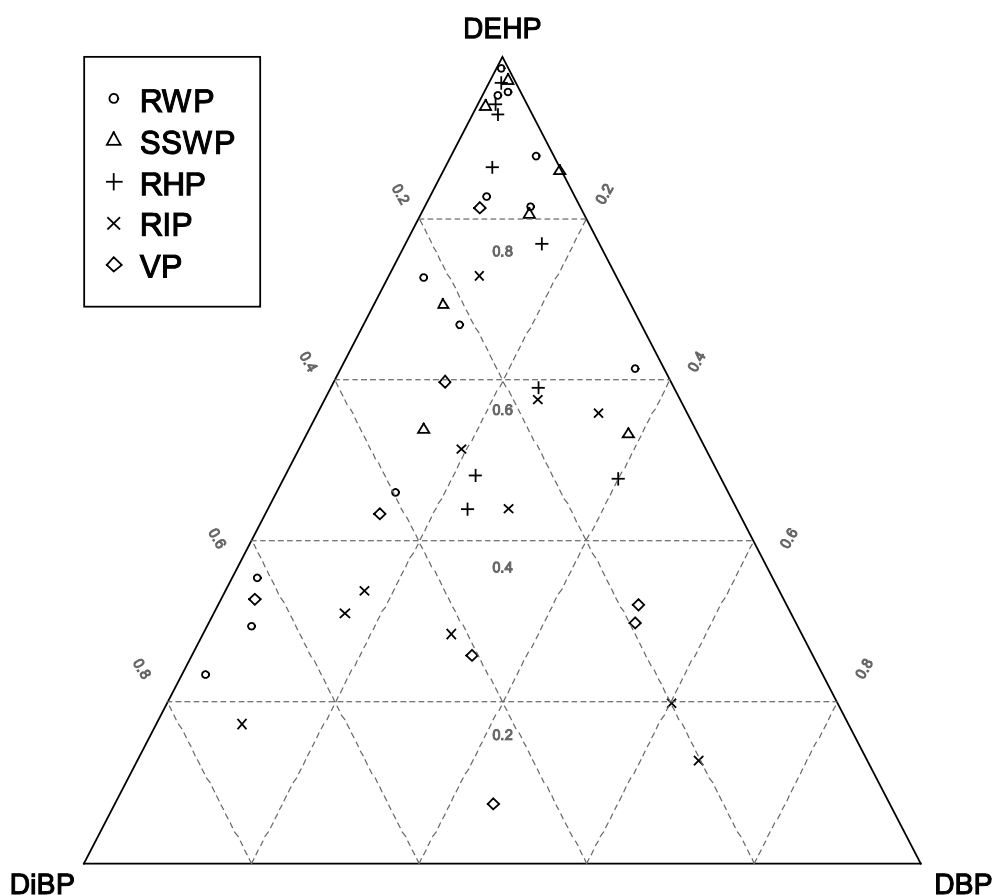
327 results are provided in Table 3 and suggest consistently that waste or recycled household plastics  
 328 were different to either recycled industrial or virgin plastics in  $ilr_1$  (see Eq. 1) coordinates, while  
 329 differences in  $ilr_2$  (see Eq. 1) coordinates were consistently insignificant. This indicated that the  
 330 ratio DiBP/DBP, on average, displayed the same behaviour in all of the groups. When combined  
 331 with the results for  $ilr_1$  coordinates, this suggested that DEHP had an important role in these  
 332 differences. To illustrate which of the three phthalates dominated the difference between the groups,  
 333 the evaluated dataset is represented in a ternary diagram (Figure 4).

334 **Table 3.** Detailed pairwise comparison of log-ratio ( $ilr$ ) coordinates (Eq. 1). Values represent the  $p$ -  
 335 values from Student's T-test. Values lower than 0.05 indicate statistically significant difference  
 336 between the two groups being compared.

	$ilr_1$		$ilr_2$	
	Recycled (Industrial)	Virgin	Recycled (Industrial)	Virgin
Residual waste	<0.01	0.01	0.39	0.75
Source-segregated waste	<0.01	0.01	0.42	0.28
Recycled (Household)	<0.01	0.01	0.62	0.34

337 It is evident from the ternary plot of the three phthalates (Figure 4) that the results for the household  
 338 plastic (i.e. RWP, SSWP and RHP) samples were dominated by DEHP, while data points for the  
 339 last two groups (i.e. RIP and VP) were either scattered (with an increasing trend towards DEHP) or  
 340 exhibited dominance favouring either DiBP or DBP. The significant difference in the  $ilr_1$  (Table 3)  
 341 suggested that among the three phthalates in focus (i.e. DiBP, DEHP and DBP) DEHP was the main  
 342 one responsible for the differences between the groups. For further interpretation, data points in the  
 343 ternary plot (Figure 4) had to be projected from the DiBP vertex (or DBP vertex) towards the  
 344 DEHP-DBP edge (or DEHP-DiBP edge). This projection showed that samples in the first three  
 345 groups (i.e. RWP, SSWP and RHP) had separated from the last two groups (i.e. RIP and VP). On  
 346 the other hand, the non-significant difference in the  $ilr_2$  (Table 3) suggested that all five groups (i.e.

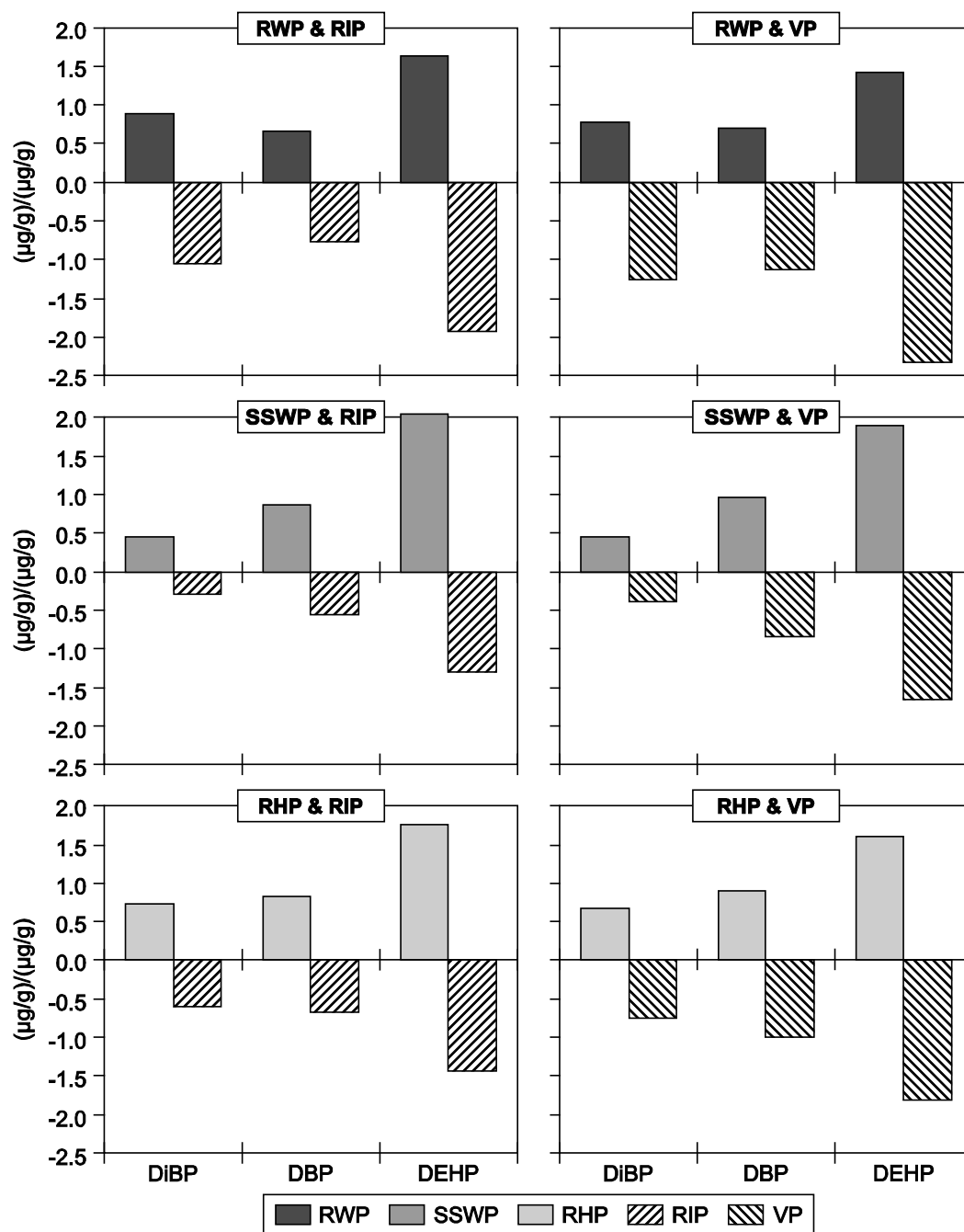
347 plastic sources) were not well separated in the sub-composition (DiBP, DBP), i.e. there were no  
 348 significant differences in the DiBP/DBP ratio. Indeed, when the data from the DEHP vertex were  
 349 projected to the DiBP-DBP edge, all the groups overlapped and did not separate clearly.



351 **Figure 4.** Ternary plot of plastics composition with respect to DiBP, DEHP, and DBP for the  
 352 samples of five plastic sources (RWP, SSWP, RHP, RIP and VP).

353 Finally, when the arithmetic mean of ilr coordinates of a group is transformed back, the geometric  
 354 mean of the original data is obtained. The geometric mean barplot in Figure 5 provides a further  
 355 illustration of the differences between two individual groups (Martín-Fernández et al., 2015). For  
 356 each plot (Figure 5), each of the bars represents the ratio (logarithmic scale) between the geometric  
 357 mean of an individual group and the combined geometric mean of the two groups being compared.  
 358 As a consequence, positive ( $> 0$ ) bars for a group (e.g. RWP in Figure 5) indicate higher phthalate

359 content. Moreover, the larger the bar for a specific phthalate (e.g. DEHP in Figure 5), the larger the  
360 difference between the two groups. The differences shown in Figure 5 are on a logarithmic scale;  
361 for example, a bar larger than 1 (e.g. DEHP in Figure 5) for a phthalate means that on average the  
362 samples in this group had almost double (172% or  $\exp(1) = 2.72$ ) the phthalate content compared  
363 with the combined geometric mean of the two groups. Figure 5 clearly illustrates higher phthalate  
364 content (i.e. positive bars) in RWP, SSWP and RHP when compared to RIP or VP (i.e. negative  
365 bars) as well as the clear dominance of DEHP (i.e. the largest differences in Figure 5). Hence, the  
366 significant difference between the first three groups (RWP, SSWP and RHP) and recycled industrial  
367 and virgin plastics (as pointed out in the results for Step 2) was mainly due to differences in DEHP  
368 content. This conclusion was previously suggested by the Student's T-test for ilr coordinates (Table  
369 3) and corroborated through the ternary diagram (Figure 4).



370

371 **Figure 5.** Geometric mean barplots comparing the groups (i.e. sources of plastics) with statistically  
 372 significant difference among them  $[(\mu\text{g/g})/(\mu\text{g/g})]$ . Each bar represents the ratio (logarithmic scale)  
 373 between the geometric mean of an individual group and the combined geometric mean of the two  
 374 groups being compared (Martín-Fernández et al., 2015).

375

### 376 3.3 Implications for plastics recycling

377 The statistical analysis of the experimental data for presence of phthalates in plastic samples  
378 highlighted several important issues: i) the insignificant difference between the waste plastic (RWP  
379 and SSWP) samples indicated that the household plastics collection scheme had no influence on the  
380 presence of phthalates in waste plastics (i.e. phthalate content in plastic items disposed in residual  
381 or source-segregated waste was the same); ii) the insignificant difference between household waste  
382 plastic samples (RWP and SSWP) and samples of recycled household plastics (RHP) suggested that  
383 phthalates were not removed following plastics recycling and could potentially persist in the  
384 recycling process, resulting in phthalate spreading and accumulating; iii) as no difference was  
385 detected in pre-consumer plastic samples (RIP and VP), the recycling of industrial waste plastics  
386 does not appear to significantly increase phthalate content in plastics and iv) finally, the significant  
387 difference between household plastic (RWP, SSWP, and RHP) samples and samples of pre-  
388 consumer plastics (RIP and VP) may indicate that phthalates were added in the later stages of  
389 manufacturing (labelling, gluing, etc.) or that samples of the household waste plastics were  
390 contaminated by other articles with higher phthalate content (e.g. PVC). This may lead to further  
391 contamination of recycled plastics, as achieving 100% purity when sorting household waste plastics  
392 is practically impossible (WRAP, 2010).

## 393 4. Conclusions

394 Samples of plastics from household waste, recycled waste and virgin plastics were obtained, and  
395 phthalates were identified in most of the samples. DBP, DiBP and DEHP were the most abundant  
396 phthalates, with 460 µg/g, 360 µg/g and 2700 µg/g as the highest concentrations measured,  
397 respectively. Statistical data analysis showed that plastic resin (e.g. PET, HDPE, PS) could not  
398 explain the presence of phthalates, while the source of plastic material samples (e.g. waste plastics,

399 recycled plastics, virgin plastics) was the single factor significantly influencing phthalate content. A  
400 comparison of the five sources of samples indicated that recycling could be a potential source of  
401 phthalates in recycled plastics. When recycled plastics are used in applications sensitive to phthalate  
402 content (e.g. children's toys and food-contact articles), the source of plastics and their chemical  
403 composition should be monitored closely. DEHP can serve as an indicator phthalate, as it was  
404 abundant in the analysed samples and was highlighted as the main factor influencing differences  
405 between the evaluated sources of plastics.

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